The normal vibrations of formic acid and methyl formate

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Abstract—Normal coordinate calculations have been carried out for methyl formate and formic acid on the basis of three different simplified harmonic force fields. The infrared spectra of $DCOOCD_3$ were obtained and the fundamental modes were assigned. The isotopic species HCOOH, DCOOH, HCOOD, DCOOD, $HCOOCH_3$, $DCOOCH_3$, $HCOOCD_3$ and $DCOOCD_3$ were included in least squares refinements of force constants. Force constants associated with the H(CO)O grouping were assumed to be transferable from the acid to the ester. Calculations were carried out with a Urey–Bradley force field, a valence-type force field derived solely from observed frequencies, and a valence-type force field with carbon–oxygen stretching constants evaluated from bond length data. The average error for 90 observed frequencies was 8 cm^{-1} (~0.7%) for the Urey–Bradley force field and below 6 cm^{-1} (~0.6%) for the valence-type force fields. The calculations revealed that the use of deuterated species does not provide sufficient data to obtain values for important skeletal interaction constants. Utilization of bond length data led to a reasonably complete force field, to acceptable values of interaction constants and to a good agreement between observed and calculated frequencies. Application of the Urey–Bradley approximation resulted in C=O and C—O stretching constants with apparently too low values. The calculated potential energy distribution as well as the Cartesian displacements for several modes are sensitive to the nature of the approximate force field, despite the good frequency agreement obtained with all three employed approximations. The results suggest that consideration must be given to the nature of an approximate force field before the calculated form of a group vibration is accepted as being physically meaningful.

Introduction

Over the past few years extensive normal coordinate calculations have been carried out on several groups of moderately complex organic molecules [1–4]. For some types of molecules, such as the n-paraffins [1], simple aliphatic ethers [3] and chlorinated benzenes [4], transferable simplified harmonic force fields have been proposed which reproduce the vibrational frequencies of a considerable number of related structures with fair accuracy [1, 3, 4]. Molecules containing

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[2] P. Cossee and J. H. Schachtschneider, *J. Chem. Phys.* **44,** 97 (1966).
[3] R. G. Snyder and G. Zerbi, *Spectrochim. Acta* **23A,** 391 (1967).
[4] J. R. Scherer, *Spectrochim. Acta* **19,** 601 (1963); *ibid.* **20,** 345 (1964); *ibid.* **21,** 321 (1965); *ibid.* **23A,** 1489 (1967); *ibid.* **24A,** 747 (1968).

C=O groups [2, 5–7] appear to present difficulties in all except the simplest cases. If a simplified valence force field is applied to acetone, acetaldehyde and formaldehyde, the choice of interaction constants has an appreciable influence on the magnitude of some important diagonal force constants and on the normal co-ordinates [2]. Even if many isotopic species of related molecules are subjected to simultaneous refinement, several sets of force constants can be obtained which reproduce the observed frequencies reasonably well; it is not easy to decide which one comes closest to the "actual situation in this group of molecules [2]". The arbitrariness in choosing force constants is reduced if a Urey–Bradley (UB) type force field [8–10] is employed. Unfortunately, the frequency fit is frequently not as good [1, 2, 4], the computational uncertainties tend to be higher, and modifications are often necessary which again introduce interaction constants of a partly arbitrary nature [1, 2, 11].

We have carried out vibrational analyses of $HCOOCH_3$, $DCOOCH_3$, $HCOOCD_3$, $DCOOCD_3$, HCOOH, DCOOH, HCOOD and DCOOD with several types of simplified harmonic force fields, in order to obtain additional information on moderately complex molecules with C=O groups; to explore the limitations of the usual computational procedures [1, 10] as applied to such molecules; and to obtain some understanding of the group vibrations of simple carboxylic acids and esters. Previously reported normal co-ordinate treatments of formic acid and methyl formate appear to have been carried out without a least squares refinement of force constants [12, 13], have involved only modes of one symmetry species [12, 14], or have been based on very simple potential functions [15]. The values of some reported Urey–Bradley constants change considerably from the acid [12] to the ester [13].

The geometry of formic acid [16] and of methyl formate [17] is well known from microwave data. It strongly suggests that the potential constants associated with the H—(CO)—O— grouping should be transferable from the acid to the ester. In the course of this study all eight listed isotopic species were included in the least squares refinements. Considerations based on bond length–force constant correlations [18] were used as an additional criterion. To study the effects of

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different potential functions on the form of calculated group vibrations, Cartesian displacements and their computational uncertainties [19] were obtained.

Source of Data and Vibrational Assignments

Methyl formate

Vibrational assignments have been reported for $HCOOCH_3$ [20, 21], $DCOOCH_3$ and $HCOOCD_3$ [21]. The molecules have C_s symmetry, eighteen fundamentals are divided into twelve a' and six a'' modes. The in-plane modes are relatively easily assigned on the basis of band contours and deuteration shifts [21]. Only one

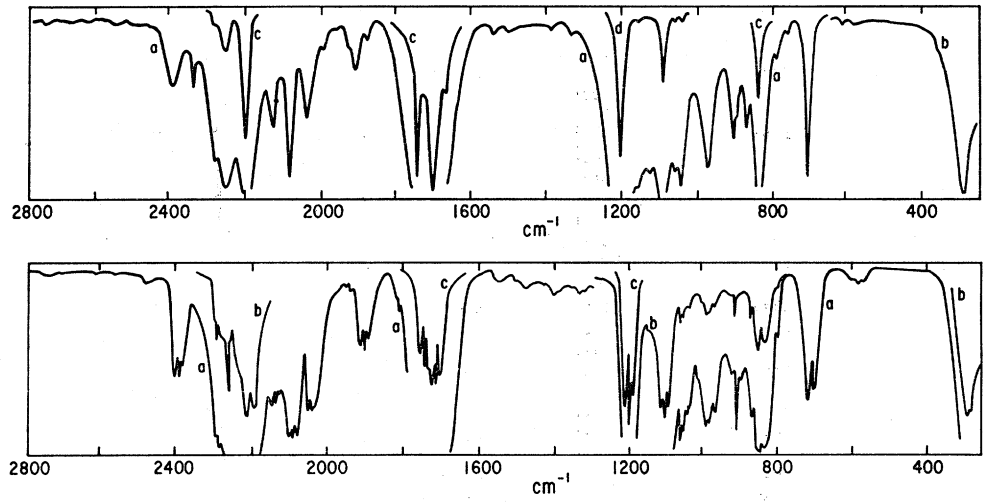

Fig. 1. Infrared spectrum of $DCOOCD_3$.
Upper curve: solution in CCl_4 (2800–950 cm^{-1}, 600–300 cm^{-1}) and CS_2 (950–600 cm^{-1}). Concentration: a, 1:10; b, 1:50; c, 1:100; d, 1:300. Path: 0.4 mm. Lower curve: Vapor in 10 cm cell. Pressure: a, 200 mm Hg; b, 35 mm Hg; c, 5 mm Hg.

assignment was inconsistent with the calculations reported below: the a' symmetric CD_3 stretching frequency. In the spectrum of $HCOOCD_3$ medium to strong bands are observed at 2214, 2135, and 2087 cm^{-1}, corresponding to two combinations and the a' fundamental. The results (see below) suggest that the unperturbed fundamental frequency is close to the middle value. The infrared spectra of $DCOOCD_3$, as obtained with a Beckman IR-7 instrument,* are shown in Fig. 1. The sample was obtained from Merck and Co., Ltd. (Canada) and showed no absorption bands of isotopic impurities. The assignments of in-plane modes, as given in Table 1, were carried out by comparison with the previously investigated isotopic species.

* Mention of commercial items is for your convenience and does not constitute an endorsement of this over similar products by the U.S. Department of Agriculture.

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Table 1. Infrared spectrum of $DCOOCD_3$, 2600–250 cm^{-1}

Solution	Gas	Int.	Type*	Assignment†
2550	2561	vw		
2538	—	vw		
2481	2480	vw		
2393	2400, 2390, 2380	m	*A*	
2337		w		
2277	2291, 2284, —	m	*A*	*a′*
2252	2259	s	*Q*	*a″*
2198	2210, 2202, 2194	s	*AB*	*a′*
2125	2143, 2134, 2127	m	*A*	*a′*
2084	2101, 2091, 2081	m	*A*	*a′*
2033	2047, 2041, 2033	m	*A*	*a′*
1906	1916, 1905, 1895	w	*A*	
1874	1875	vw		
1793	1811	vw		
1740	1757, 1746, 1737	vs	*A*	*a′*
1698	1724, 1714, 1704	vs	*A*	*a′*
1542	1549	vw		
1487	1477	vw		
1405	1403	vw		
1333	1335	vw		
1199	1212, 1201, 1191	vs	*A*	*a′*
1091	1112, 1105, 1093	s	*A*	*a′*
1056	1060	m	*Q*	*a″*
1056	1055	m	*B*	*a′*
	(1070)			
1041	1050, 1041, 1034	m	*A*	*a′*
969	964, 979	m	*B*	*a′*
903	908	m	*Q*	*a″*
867	867	m	*Q*	*a″*
834	849, 841, 832	s	*A*	*a′*
787	796	vw		
708	717, 709, 700	m	*AB*	*a′*
614		vw		
584	580	vw		
287	287	s	?	*a′*

* *Q* indicates a very sharp *Q* branch, very shallow *P* and *R* branches.
† Large bracket indicates resonance with overtones or combinations.

The out-of-plane modes present some difficulties. The bands tend to be weak and frequently show only a sharp Q branch of low intensity [21]. One previously reported a'' band with a clean PQR structure, assigned to H—C(=O)— bending [20] or CH_3 rocking [21] and centering at 1032 cm^{-1}, was identified as a methanol band. It appears upon the slightest hydrolysis of the ester. The observed a'' modes which could be identified with reasonable certainty (after rigorous repurification of the ester samples) are listed in Table 2 to provide an overall picture of the available data. Also included are a'' frequencies of formic acid (helpful to calculate values for the a'' C—H bending modes of the ester), along with the best calculated

Table 2. Out-of-plane fundamental frequencies

Approx. description*		$HCOOCH_3$	$DCOOCH_3$	$HCOOCD_3$	$DCOOCD_3$	HCOOH	DCOOH	HCOOD	DCOOD
$CH_3(CD_3)$	st	3012	3007	2258	2259				
$CH_3(CD_3)$	b	(1481)	(1481)	1060	1060				
$CH_3(CD_3)$	r	(1165)	(1165)	906	908				
CH(CD)	r	(1023)	(872)	(1028)	867	1033	(870)	(1031)	873
OH(OD)	b					638	629	508	491
COC	t	341	(300)	324	(289)				
$—CH_3(—CD_3)$	t	130	130	(95)	(95)				

* st, b, r, t—stretching, bending, rocking, torsion respectively.
The frequencies in parentheses are calculated with SYMFFII (see below).

values for the unobserved bands (cf. below). The calculated a'' CH_3 bending, CH_3 rocking and skeletal torsion frequencies overlap with very strong in-plane fundamentals (CH_3 bending and rocking, C—O—C bending). The a'' H—C(=O)— and D—C(=O)— deformations must be inherently weak.

Formic acid

The frequencies and assignments for HCOOH, DCOOH, HCOOD and DCOOD were taken from the work of MILLIKAN and PITZER [22] and MIYAZAWA and PITZER [23]. The frequencies for the lowest a' fundamentals and the a'' fundamentals are from the gas phase work described in the latter Ref. [23], the remaining frequencies from Ref. [22]. Two modifications were made in the assignments for DCOOD. (i) As suggested by NAKAMOTO *et al.* [12], the observed frequency of 1040 cm^{-1} appears too high for an a' mode involving primarily C—O—D bending. Two bands are observed in this region [24, 12], centering at 1040 cm^{-1} and around 970 cm^{-1}. They could be assigned to the a' fundamental in resonance with $2 \times \nu_9$, in analogy to the situation found in HCOOD [22]. This fundamental was given zero weight in our calculations. (ii) In the C—D stretching region, two bands of about equal intensity are observed at 2195 and 2232 cm^{-1} [24]. WILLIAMS suggested that they are caused by the fundamental in resonance with a combination band [24]. The midpoint was taken as the unperturbed fundamental frequency.

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Internal Coordinates and Choice of Force Fields

Internal coordinates were defined as indicated in Fig. 2. The Greek letters designating bond angles were chosen in analogy to Ref. [2]. The numbering of the coordinates of the H(CO)O grouping is identical for the acid and the ester. For molecules containing well-defined groupings such as $-CH_3$, the vibrational problem is frequently set up and force constants are reported in terms of commonly accepted

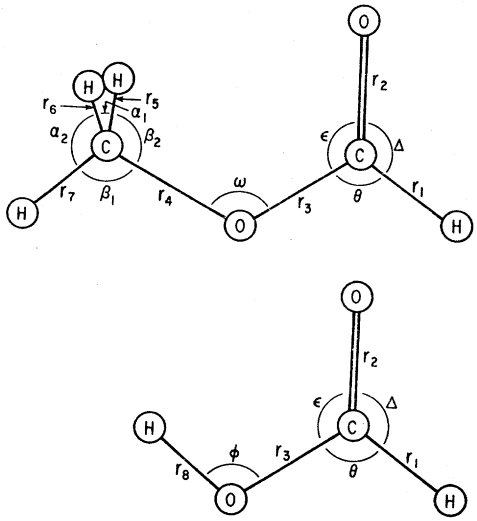

Fig. 2. Internal coordinates for methyl formate and formic acid.

sets of symmetry coordinates [25–28]. The symmetry coordinates are listed and defined in Table 3. The redundancy in S_{6a} and S_{6b} was removed by an orthogonal transformation of the form [25, 28]:

$$S_6 = P \cdot S_{6a} - Q \cdot S_{6b}$$
$$S_0 = Q \cdot S_{6a} + P \cdot S_{6b} \equiv 0$$

where P and Q are functions of the bond angles α and β [25, 28]. For tetrahedral geometry $P = 1$, $Q = 0$; for the geometry reported by Curl [17] for methyl formate, $P = 0.999716$ and $Q = 0.023802$.

Force constants were calculated in symmetry coordinate space (SYMFF) and Urey–Bradley coordinate space (UBFF). For the studied molecules the former appears to have some advantages over a valence force field (VFF): redundancies are removed in a well defined manner; it appears to be easier to choose significant interaction constants; force constant values associated with the CH_3 group can be compared with a variety of molecules [25–28].

For calculations carried out with a SYMFF (or a VFF) on all except very simple molecules, it is not easy to decide which off diagonal constants should be included

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in a constrained force field [1–4]. Starting with a very simple force field, interaction constants were added one by one and judged by the resulting improvements in frequencies; by the "reasonableness" [2] of the values; and by the computational uncertainties. (Although the latter do not reflect the correctness of a model [19], they do indicate what can or cannot be reasonably determined.) Based on these criteria, a set of symmetry force constants was evaluated which contained a minimum number of off diagonal terms (SYMFFI). The specific choice is briefly discussed further below.

Table 3. Symmetry coordinates

	Definition	Description*		Applies to: A—acid E—ester
a'	$S_1 = 6^{-1/2}(2r_7 - r_6 - r_5)$	CH_3	as	E
	$S_2 = 3^{-1/2}(r_5 + r_6 + r_7)$	CH_3	ss	E
	$S_3 = r_1$	HC	s	E, A
	$S_4 = r_2$	C=O	s	E, A
	$S_5 = 6^{-1/2}(2\alpha_1 - \alpha_2 - \alpha_3)$	CH_3	ab	E
	$S_{6a}\dagger = 6^{-1/2}(\Sigma\alpha - \Sigma\beta)$	CH_3	sb	E
	$S_{6b}\dagger = 6^{-1/2}(\Sigma\alpha + \Sigma\beta)$			
	$S_7 = 2^{-1/2}(\Delta - \theta)$	HC	r	E, A
	$S_8 = 6^{-1/2}(2\beta_1 - \beta_2 - \beta_3)$	CH_3	r	E
	$S_9 = r_3$	C—O	s	E, A
	$S_{10} = r_4$	O—CH_3	s	E
	$S_{11} = 6^{-1/2}(2\varepsilon - \Delta - \theta)$	COO	b	E, A
	$S_{12} = \omega$	COC	b	E
	$S_{13} = \tau_3$	OH	s	A
	$S_{14} = \varphi$	COH	b	A
	$S_0' = 3^{-1/2}(\varepsilon + \Delta + \theta)$	H(CO)O	redun.	E, A
a''	$S_{15} = 2^{-1/2}(r_5 - r_6)$	CH_3	as	E
	$S_{16} = 2^{-1/2}(\alpha_2 - \alpha_3)$	CH_3	ab	E
	$S_{17} = 2^{-1/2}(\beta_2 - \beta_3)$	CH_3	r	E
	$S_{18}\ddagger = \gamma$	H—C	b	E, A
	$S_{19} = \tau_1$	skel.	t	E
	$S_{20} = \tau_2$	CH_3	t	E
	$S_{21} = \tau_3$	—C(=O)—O—H	t	A

* as, asymmetric stretch; ss, symmetric stretch; s, stretch; b, bend; r, rock; t, torsion.

† $S_6 = P \cdot S_{6a} - Q \cdot S_{6b}$; $S_0 = Q \cdot S_{6a} + P \cdot S_{6b}$; see text.

‡ The signs of the a'' symmetry coordinates were defined so that the cross terms in the $\mathscr{G}$ matrix had the following signs: (15, 16)(+), (15, 17)(−), (15, 19)(−), (15, 20)(−), (16, 17)(+), (16, 19)(−), (16, 20)(−), (17, 18)(−), (17, 19)(+), (17, 20)(+), (18, 19)(−), (18, 20)(+), (18, 21)(−), (19, 20)(−). Based on Fig. 2, for S_{18} the displacement is positive if the H atom moves up; for S_{19} and S_{21} the carbonyl oxygen moves up; for S_{20} the carbonyl carbon moves up.

Recently, detailed empirical relationships have been proposed between some bond stretching force constants and bond lengths [18, 29]. If the C=O and C—O stretching constants are assigned fixed values as calculated by the procedure of LADD *et al.* [18] (the values are very close to the ones obtained with SYMFFI), a much more complete force field can be obtained (SYMFFII). For the —(CO)—O—C skeleton stretch–stretch interactions (one common atom) and stretch–bend interactions (two common atoms) were included and could be evaluated with a reasonably low computational uncertainty.

Calculations with a UBFF were carried out in the usual manner [4, 10]. Only

Table 4A. Diagonal symmetry force constants

	SYMFF I	Dispersion	SYMFF II	Dispersion	SYMFF (UB)
$F(1)$	4.918	0.018	4.919	0.015	5.002
$F(2)$	5.092	0.023	5.091	0.020	5.061
$F(3)$	4.690	0.014	4.681	0.015	4.815
$F(4)$	12.426	0.199	12.300	—	11.439
$F(5)$ } $F(16)$}	0.518	0.004	0.517	0.004	0.524
$F(6)$	0.683	0.009	0.679	0.007	0.695
$F(7)$	0.618	0.009	0.620	0.008	0.639
$F(8)$ } $F(17)$}	0.868	0.014	0.871	0.011	0.850
$F(9)$	6.177	0.155	6.570	—	5.760
$F(10)$	4.246	0.134	4.370	—	4.830
$F(11)$	1.261	0.044	1.222	0.040	1.541
$F(12)$	1.624	0.079	1.479	0.062	1.358
$F(13)$	7.164	0.022	7.165	0.019	7.190
$F(14)$	0.681	0.018	0.648	0.018	0.668
$F(15)$	4.820	0.017	4.820	0.015	4.899
$F(18)$	0.466	0.014	0.466	0.013	0.466
$F(19)$	0.187	0.008	0.187	0.007	0.189
$F(20)$	0.032	0.004	0.032	0.003	0.032
$F(21)$	0.167	0.004	0.167	0.004	0.167

Stretching force constants: mdyn/Å.
Bending force constants: mdyn · Å/rad².

Table 4B. Off diagonal symmetry force constants

	SYMFFI	Dispersion	SYMFFII	Dispersion
$f(4, 7)$	0.676	0.100	0.392	0.157
$f(4, 11)$	0.723	0.133	0.560	0.201
$f(6, 10)$	−0.534	0.044	−0.530	0.034
$f(7, 9)$	−0.328	0.037	−0.240	0.055
$f(9, 14)$	−0.322	0.040	−0.280	0.044
$f(8, 9)$	0.407	0.046	0.223	0.043
$f(8, 10)$	0.162	0.042	0.204	0.038
$f(11, 14)$	−0.066	0.014	−0.118	0.017
$f(18, 19)$	0.098	0.021	0.098	0.018
$f(18, 21)$	0.096	0.020	0.096	0.018
$f(7, 11)$	—	—	0.068	0.025
$f(7, 14)$	—	—	0.067	0.021
$f(9, 10)$	—	—	0.247	0.118
$f(9, 11)$	—	—	0.265	0.075
$f(9, 12)$	—	—}	0.240	0.059
$f(10, 12)$	—	—}		
$f(4, 9)$	—	—	0.545	0.340

Units as in Table 4A. Stretch–bend interactions: mdyn/rad.

gem interactions and the *cis* OCOH interaction of formic acid could be determined. The number of non-UB constants was held at a minimum, to provide information regarding the applicability of the UB approximation to these molecules. To obtain a reasonable frequency fit for the a'' modes, one non-UB interaction constant was necessary for the acid and one for the ester (H—C(=O)—wagging, skeletal torsion).

The potential energy, 2V, for the symmetry valence force fields is defined by the force constants listed in Table 4 in conjunction with the defined coordinates as listed in Table 3. The potential energy function for UB calculations is defined in the usual manner [4, 9, 10]. The assumption was made that $F' = -0{\cdot}1\,F$ and $C' = -0{\cdot}1\,C$ for all repulsive interactions.

Methods of Computation

The computational procedures for solving the vibrational secular equation on the basis of Wilson's **GF**-matrix formulation, and for evaluating UBFF and VFF potential constants by applying the least squares criterion, have been described by several authors [1, 10, 28, 30, 31]. A recent concise summary appears in Ref. [31]. Using a nomenclature based on Ref. [1], the kinetic energy matrices were diagonalized by

$$\tilde{\mathrm{A}}\mathscr{G}\mathrm{A} = \Gamma$$

where $\mathscr{G}$ is in symmetry coordinates. For calculations in symmetry coordinates the matrices **W** and **H** are defined as

$$\mathbf{W} = \mathbf{A}\Gamma^{1/2}$$

$$\mathbf{H} = \tilde{\mathbf{W}}\mathscr{F}\mathbf{W}$$

The frequency parameters are given by

$$\mathbf{HC} = \mathbf{C}\Lambda$$

and the transformation from normal coordinates to symmetry coordinates:

$$\mathbf{S} = \mathscr{L}\mathbf{Q}$$

where

$$\mathscr{L} = \mathbf{WC}$$

For UBFF calculations the elements of the potential energy matrix **F** in general valence coordinates (including redundancies) are given by:

$$F_{k,l} = \sum_j Z^j_{k,l}\varphi_j$$

where $\vec{\varphi}$ is a vector of the UB force constants. The $\mathscr{G}$ matrix was retained in symmetry coordinates and **W*** was defined as:

$$\mathbf{W}^* = \tilde{\mathbf{U}}\mathbf{A}\Gamma^{1/2} = \tilde{\mathbf{U}}\mathbf{W}$$

Thus,

$$\mathbf{H} = \tilde{\mathbf{W}}^*\mathbf{F}\mathbf{W}^* = \tilde{\mathbf{W}}\mathscr{F}\mathbf{W}$$

and

$$\mathbf{HC} = \mathbf{C}\Lambda$$

U is the orthogonal transformation from internal coordinates **R** to symmetry coordinates **S**.

Least squares refinements were carried out in the usual manner [1, 10], assigning all observed frequencies a weight of $1/\lambda$ (observed) and unobserved frequencies a weight zero. A total of ninety observed frequencies of the eight molecules were used to refine the potential functions. The solutions obtained for SYMFFI and II were not influenced by (reasonable) variations in the initial values of the force constants subjected to refinement. For UBFF calculations the starting value of

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[31] J. N. Gayles, Jr., W. T. King and J. H. Schachtschneider, *Spectrochim. Acta* **23A**, 703 (1967).

the O---O repulsive constant appears to be important. With a value of 1.5 mdyn/Å [13] no stable solution could be obtained. With a value of 0.5 mdyn/Å the iterations rapidly converged to the values given in Table 5. To compare the results obtained by refining UB force constants with the results obtained in symmetry coordinate space, the former were also transformed into symmetry coordinate space.

Potential energy distributions (PED) and Cartesian displacements were obtained as usual [4]. The computational significance of the latter quantities depends on the uncertainties of the estimated force constants, i.e., the force constant moment matrix $\mathbf{M}^{(\varphi)}$ [19]. The uncertainties in vibrational amplitudes were calculated from the inverse of the normal equations of the least squares refinement of force constants, as previously described [19]. For the constrained force field SYMFFII unreasonably low dispersions would be obtained for modes associated with the fixed C=O and C—O stretching constants. To avoid the illusion that any displacement vectors could be obtained with precision on the basis of available data, diagonal elements of $\mathbf{M}^{(\varphi)}$ corresponding to the fixed constants were taken from the results with SYMFFI. The reverse procedure was applied to some fixed constants of SYMFFI, i.e., the $M_{ii}^{(\varphi)}$ were taken from SYMFFII.

The numerical computations were carried out with previously employed computer programs [4, 19] on the IBM 7040 computer at the University of Pennsylvania Computing Center. The FORTRAN programs were slightly modified to comply with the FORTRAN IV language and to calculate a $\mathbf{W}$ matrix for computations in symmetry coordinates.

Results and Discussion

The obtained symmetry force constants and their dispersions are listed in Table 4, the Urey–Bradley force constants in Table 5, observed and calculated frequencies in Table 6.

Symmetry valence force fields

Under the heading SYMFFI Tables 4A and 4B list the force constants obtained in a calculation where all non-zero values were refined on the basis of the frequencies of the eight studied molecules. The choice of interaction constants is admittedly somewhat arbitrary. There are a total of ten such constants. Four involve the CH_3 group and apply only to the ester; three involve the OH linkage and apply only to the acid; three are associated with the H—(CO)—O— grouping and apply to both. A brief dissussion concerning the choice of these particular terms follows.

$f(4, 7)$, $f(4, 11)$, and $f(7, 9)$ represent stretch–bend interactions in the H—(CO)—O— grouping and appeared indispensable for obtaining reasonably good calculated frequencies. $f(6, 10)$ is important in most X—CH_3 molecules and implies that stretching of the C—X bond tends to open the CH_3 umbrella [25, 28]. $f(8, 9)$ and $f(8, 10)$ are nesessary to fit the in-plane CH_3 rocking and the C—O stretching frequencies. Qualitative evidence indicates that these modes are

Table 5. Urey–Bradley force constants

	Value	Dispersion
Stretching		
K(O—H)	7.004	0.063
K(H—C(=O)—)	4.242	0.106
K(CH), (r_5)	4.460	0.043
K(CH), (r_7)	4.615	0.038
K(C=O)	10.717	0.258
K(C—O)	4.358	0.421
K(O—CH_3)	2.328	0.247
Bending		
H(HCH)	0.500	0.012
H(OCH)$_\beta$	0.356	0.026
H(OCH)$_\theta$	0.505	0.176
H(COH)	0.647	0.075
H(H—C=O)	0.355	0.130
H(OCO)	1.771	0.255
H(COC)	0.591	0.170
Repulsive		
F(H- -H)$_\alpha$	0.051	0.023
F(O- -H)$_\beta$	0.795	0.049
F(O- -H)$_\theta$	0.461	0.164
F(C- -H)$_\varphi$	0.382	0.135
F(H- -O)$_\Delta$	0.413	0.164
F(O- -O)	0.482	0.124
F(C- -C)	1.107	0.295
C(O- -H)$_{\varepsilon,\varphi}$	−0.194	0.026
Out-of-plane*		
f_γ	0.466	0.019
$f_{\tau(1)}$	0.189	0.011
$f_{\tau(2)}$	0.032	0.005
$f_{\tau(3)}$	0.167	0.006
$f_{\gamma,\tau(1)}$	0.095	0.026
$f_{\gamma,\tau(3)}$	0.096	0.027

* Nomenclature as in Table 3. Units as in Table 4.

Table 6. Observed and calculated frequencies and average errors

	$\Delta\tilde{\nu}$ (cm^{-1}) Obs. freq. (cm^{-1})	8.1 (0.65%) UB	5.9 (0.59%) SYMFFI	5.1 (0.52%) SYMFFII	Error (SYMFFII)
	HCOOH				
1	3570.0	3585.4	3583.6	3583.7	−13.7
2	2943.0	2955.8	2943.9	2942.1	0.9
3	1770.0	1774.9	1775.8	1775.1	−5.1
4	1387.0	1371.6	1381.9	1382.8	4.2
5	1229.0	1243.8	1236.6	1238.4	−9.4
6	1105.0	1110.6	1118.3	1118.8	−13.8
7	625.0	626.9	630.1	632.9	−7.9
8	1033.0	1035.5	1035.7	1035.8	−2.8
9	638.0	640.3	640.3	640.3	−2.3
	DCOOH				
1	3570.0	3585.3	3583.5	3583.7	−13.7
2	2220.0	2199.8	2206.8	2210.6	9.4
3	1756.0	1728.9	1751.8	1747.1	8.9
4	0.0	1244.9	1255.8	1240.5	0.0
5	1143.0	1138.2	1125.8	1140.4	2.6
6	970.0	968.9	962.6	965.5	4.5
7	620.0	624.2	625.7	627.7	−7.7
8	0.0	871.7	871.8	871.8	0.0
9	629.0	631.7	631.8	631.8	−2.8

Table 6 (*cont.*)

	Obs. freq. (cm^{-1})	UB	SYMFFI	SYMFFII	(SYMFFII)
	HCOOD				
1	2947.0	2955.7	2943.9	2942.1	4.9
2	2632.0	2610.6	2613.0	2612.8	19.2
3	1772.0	1772.4	1765.7	1768.8	3.2
4	0.0	1368.1	1377.3	1371.9	0.0
5	1178.0	1150.8	1149.1	1172.6	5.4
6	990.0	975.3	987.6	984.2	5.8
7	562.0	556.1	555.4	551.0	11.0
8	0.0	1032.6	1032.8	1032.8	0.0
9	508.0	504.2	504.2	504.2	3.8
	DCOOD				
1	2632.0	2610.5	2613.1	2612.9	19.1
2	2213.0	2198.7	2205.8	2209.4	3.6
3	1742.0	1727.3	1742.1	1741.6	0.4
4	1171.0	1171.4	1177.8	1168.7	2.3
5	0.0	996.4	994.3	1027.8	0.0
6	945.0	951.4	947.5	936.0	9.0
7	558.0	554.6	553.2	548.5	9.5
8	873.0	871.1	871.2	871.2	1.8
9	491.0	488.2	488.3	488.3	2.7
	$HCOOCH_3$				
1	3045.0	3056.0	3046.7	3046.9	−1.9
2	2969.0	2956.7	2968.0	2968.0	1.0
3	2943.0	2953.3	2945.0	2942.8	0.2
4	1754.0	1774.9	1756.5	1758.4	−4.4
5	1465.0	1473.3	1471.4	1472.1	−7.1
6	1445.0	1446.2	1447.2	1445.1	−0.1
7	1371.0	1372.7	1374.7	1372.7	−1.7
8	1207.0	1211.2	1225.2	1219.5	−12.5
9	1168.0	1166.2	1167.1	1169.4	−1.4
10	925.0	927.6	928.2	927.5	−2.5
11	767.0	769.7	766.5	772.7	−5.7
12	325.0	316.6	316.8	318.2	6.8
13	3012.0	3023.9	3014.6	3014.6	−2.6
14	0.0	1476.2	1480.9	1480.5	0.0
15	0.0	1149.7	1163.8	1165.7	0.0
16	0.0	1033.1	1031.1	1030.5	0.0
17	341.0	339.5	337.8	337.7	3.3
18	130.0	130.6	130.2	130.2	−0.2
	$DCOOCH_3$				
1	3041.0	3056.1	3046.6	3046.8	−5.8
2	2967.0	2953.3	2968.0	2968.0	−1.0
3	2216.0	2201.5	2209.6	2211.9	4.1
4	1732.0	1729.9	1732.7	1730.4	1.6
5	1468.0	1473.1	1470.4	1472.0	−4.0
6	1441.0	1445.5	1446.7	1444.3	−3.3
7	1213.0	1213.4	1211.9	1208.1	4.9
8	1157.0	1165.1	1166.0	1159.1	−2.1
9	1048.0	1050.6	1050.7	1055.2	−7.2
10	878.0	872.0	886.7	878.7	−0.7
11	762.0	765.8	746.5	759.1	2.9
12	304.0	315.9	316.2	317.6	−13.6
13	3007.0	3023.9	3014.6	3014.6	−7.6
14	0.0	1476.1	1480.8	1480.5	0.0
15	0.0	1149.4	1163.6	1165.5	0.0
16	0.0	877.3	874.4	873.6	0.0
17	0.0	300.9	299.7	299.8	0.0
18	130.0	130.2	129.8	129.9	0.1

Table 6 (*cont.*)

	Obs. freq. (cm^{-1})	UB	SYMFFI	SYMFFII	Error (SYMFFII)
	$HCOOCD_3$				
1	2931.0	2956.7	2945.0	2942.9	−11.9
2	2284.0	2264.3	2278.6	2278.4	5.6
3	0.0	2116.8	2132.6	2132.8	0.0
4	1754.0	1774.7	1755.5	1758.2	−4.2
5	1368.0	1373.2	1374.9	1373.0	−5.0
6	1210.0	1215.2	1218.6	1210.8	−0.8
7	1102.0	1103.3	1096.9	1100.4	1.6
8	1063.0	1053.8	1052.6	1050.7	12.3
9	987.0	977.3	979.8	980.7	6.3
10	877.0	875.6	868.9	875.8	1.2
11	714.0	714.4	717.5	716.5	−2.5
12	305.0	290.7	291.5	292.9	12.1
13	2258.0	2242.6	2251.5	2251.6	6.4
14	1060.0	1059.4	1062.3	1061.9	−1.9
15	0.0	1033.5	1030.8	1030.1	0.0
16	906.0	895.2	900.4	902.0	4.0
17	324.0	328.5	327.0	327.0	−3.0
18	0.0	95.6	95.3	95.4	0.0
	$DCOOCD_3$				
1	2284.0	2264.7	2279.4	2279.0	5.0
2	2202.0	2201.1	2208.8	2211.2	−9.2
3	0.0	2116.7	2132.6	2132.8	0.0
4	1730.0	1729.7	1731.3	1730.2	−0.2
5	1201.0	1217.1	1202.7	1189.9	11.1
6	1105.0	1105.0	1099.0	1101.9	3.1
7	1062.0	1053.8	1059.8	1056.0	6.0
8	1041.0	1038.1	1034.6	1041.4	−0.4
9	972.0	971.0	972.5	970.7	1.3
10	841.0	834.5	835.5	837.8	3.2
11	709.0	711.7	703.8	707.5	1.5
12	287.0	290.0	290.9	292.4	−5.4
13	2259.0	2242.6	2251.5	2251.6	7.4
14	1060.0	1057.4	1060.1	1059.7	0.3
15	908.0	910.3	912.1	913.0	−5.0
16	867.0	863.6	863.8	863.7	3.3
17	0.0	289.6	288.6	288.6	0.0
18	0.0	95.4	95.1	95.1	0.0

strongly coupled [21]. (See also Figs. 3 and 4.) The in-plane formic acid interactions f (7, 14) and f (11, 14) were included to obtain reasonable in-plane frequencies for the four formic acid isotopes. f (18, 21) (formic acid) and f (18, 19) (methyl formate) involve the out-of-plane H—C bending coordinate and neighboring skeletal torsion. Deletion of any of these terms had a significant negative effect on the frequency agreement. Additional terms did not improve it. Alternative combinations resulted in poorer calculated frequencies and/or unacceptably high uncertainties.

Some aspects of the results as obtained with SYMFFI should be pointed out. First, the frequency agreement is as good (or better) as could reasonably be expected within the harmonic approximation. Attempts to calculate additional terms without additional data would therefore be meaningless. Second, the C=O, C—O and O—CH_3 stretching constants are in reasonable agreement with values obtained from bond length data on the basis of Refs. [16–18]. (12.43 $\pm$ 0.20, 6.18 $\pm$ 0.16, 4.25 $\pm$ 0.13 vs. 12.30, 6.57, 4.37). Third, the model has serious

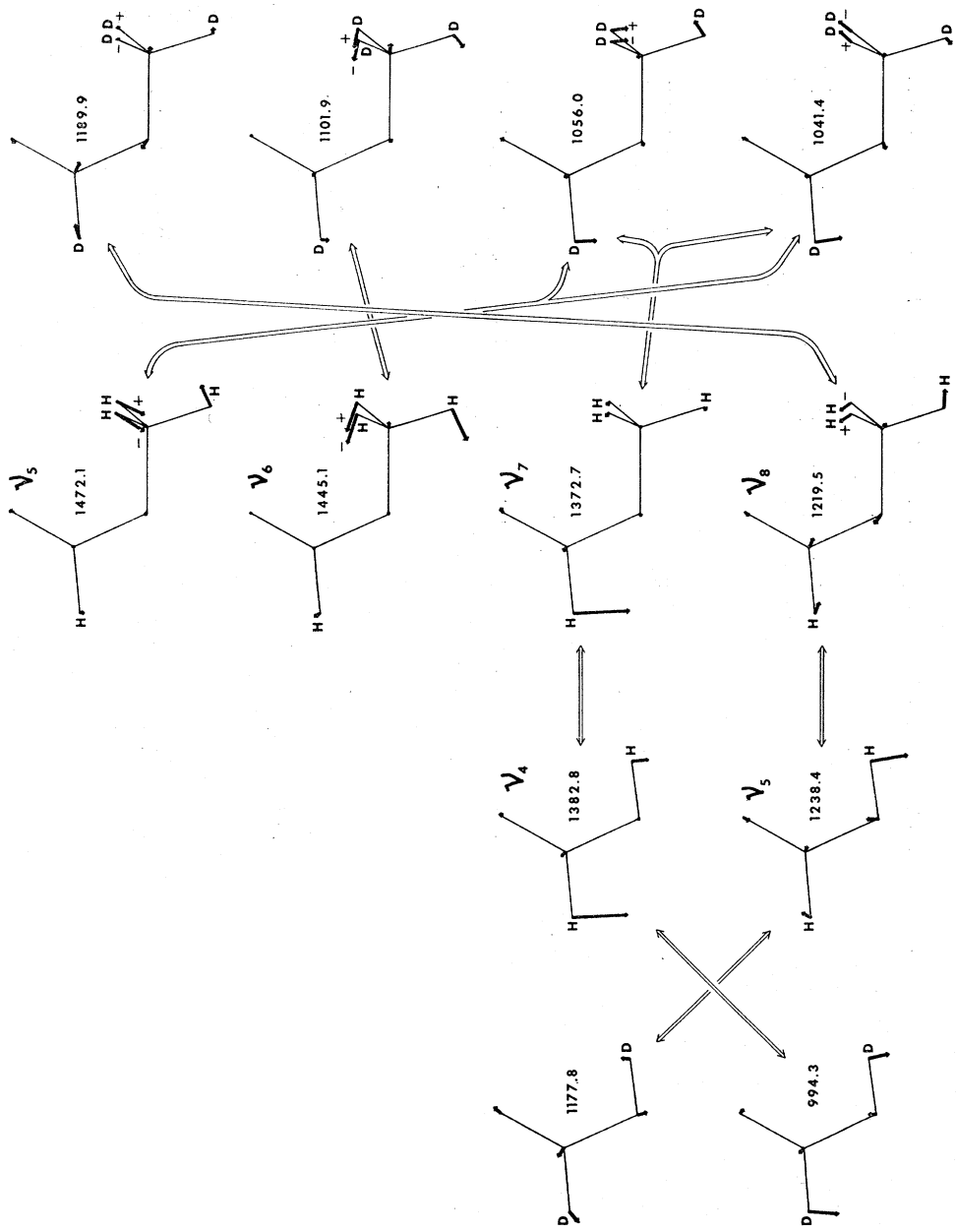

Fig. 3. Cartesian displacements for ν_5–ν_8 of methyl formate and ν_4, ν_5 of formic acid, based on SYMFFII. Broad arrows indicate the relationship between similar modes and reflect the nature of coupling in different species. The + and − signs refer to directions of displacement vectors relative to the plane of the drawing.

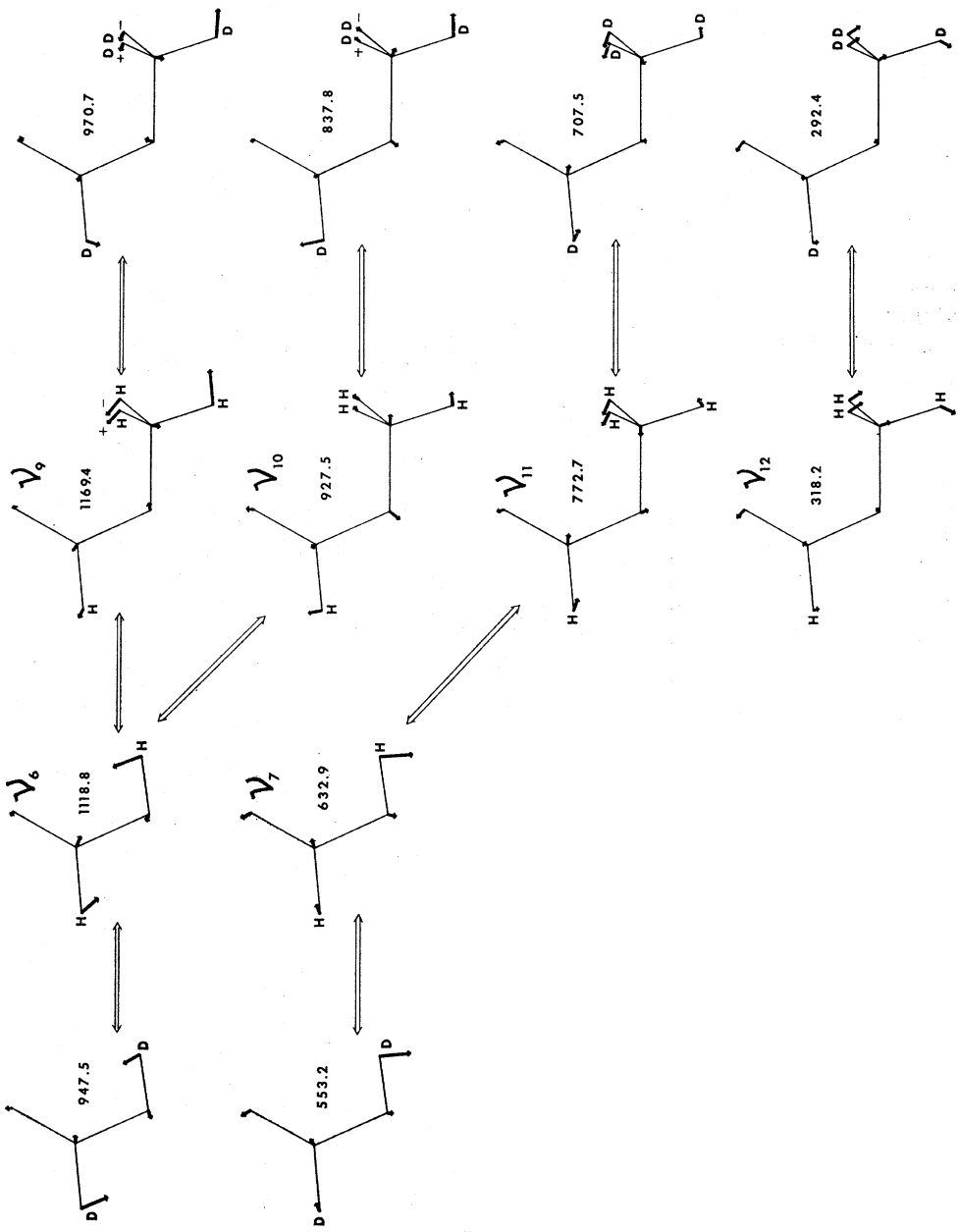

Fig. 4. Cartesian displacements for ν_9–ν_{12} of methyl formate and ν_6, ν_7 of formic acid. Broad arrows and +, − signs as in Fig. 3. Based on SYMFFII.

deficiencies because it is physically unreasonable to assume that potential energy terms such as stretch–stretch and stretch–bend interactions in the COC and OCO groupings have zero values. These latter constants could not be determined because isotopic substitution by deuteration does not sufficiently change the frequencies of "skeletal modes" [3, 11].

In calculations with SYMFFII the values for C=O and C—O stretching constants were not submitted to refinement. The results just described suggest that bond length–force constant correlations (based on very simple molecules) provide values which, in a semi-quantitative way, are applicable to larger molecules. In the absence of other data, they furnish a way to judge the reasonableness of severely constrained force fields. Conversely, if these values are not submitted to refinement it becomes possible to evaluate additional off diagonal terms in the $\mathscr{F}$ matrix.

In SYMFFII, $F(4)$, $F(9)$ and $F(10)$ (cf. Tables 3 and 4) were assigned fixed values (as obtained by Refs. [16–18]) and additional terms were added to the potential energy function. For formic acid all interaction constants were included, except the ones involving CH and/or OH stretching, and the constant f (4, 14) (C=O str., COH bend) which could not be determined. The terms associated with the H—(CO)—O grouping were also used for methyl formate; stretch–stretch and stretch–bend interactions for the COC linkage were added. SYMFFII is thus reasonably complete for formic acid and also includes the most important interactions of the methyl formate skeleton.

The results are given in Tables 4A and 4B and Table 6. The frequency agreement is slightly better than with SYMFFI, and the distribution of errors slightly more uniform. Appreciable errors only occur with CH and OH stretching modes, where anharmonicity effects can be expected to be highest. The overall average frequency error is ~ 5 cm^{-1} (0·52%). Best agreement is observed with per-deutero molecules, as expected. It is interesting to note that the interactions involving the C=O stretching mode are relatively high, i.e., the carboxyl C=O stretching mode is far from "separable" as far as the potential energy interactions are concerned.

Urey–Bradley force field

A set of refined Urey–Bradley force constants is listed in Table 5. For molecules containing skeletal segments such as C—C—C, it is frequently difficult to obtain values for the corresponding *gem* interaction constants [1, 2, 11]. Acetone provides an example [2, 11]. In the case of methyl formate and formic acid similar difficulties are encountered with the *gem* interactions F(OCO) and F(COC). The reasons are analogous to the ones encountered with SYMFFI: insufficient data concerning skeletal modes. Trial calculations revealed that a stable solution leading to reasonable results is obtained if a starting value of 0·5 mdyn/Å is assigned to F(OCO) and 1·0 mdyn/Å to F(COC). Calculations were also carried out which included additional UB-constants such as the *cis* interactions C(O=C—O—C) and C(C—O—C—H) for methyl formate. Their values could not be determined.

To provide a comparison between the two types of force fields (SYMFF and UBFF) the results of the Urey–Bradley calculations were transformed into symmetry coordinates. The resulting diagonal F_{ii} constants are included in

Table 4A. (Inclusion of the corresponding $F_{i,j}$ terms would have made Table 4B unreasonably unwieldy.) For many diagonal constants the agreement between SYMFFII and SYMFF(UB) is reasonably good. Major discrepancies involve the C=O, C—O and O—CH_3 stretching constants $F(4)$, $F(9)$, $F(10)$, and the OCO and COC bending constants $F(11)$, $F(12)$. The discrepancies do not necessarily reflect a basic inadequacy of the UB approximation. The amount of data is not sufficient to produce a well-defined solution. It should be pointed out, nevertheless, that the shallow minimum obtained by refinement in UB coordinates leads to skeletal force constants which differ substantially from best estimates by other procedures. The weaknesses of the different types of approximations are well illustrated by considering the overall results. Valence type force fields (without additional assumptions or data) do not yield values for several important interaction terms. On the other hand, the force constants obtained through the UB approximation are not independent (because of the nature of the **Z** matrix). If a single hybridization-type interaction occurs, a number of elements will be influenced and the refinement produces a "compromise" solution. For the studied molecules the frequency agreement is better and the computational uncertainties are lower for valence type force fields. Similar observations have been reported for other systems of moderate complexity [1, 2, 4].

Valence force constants for the O—CH_3 *group*

To permit a rough comparison with related data presented in internal valence coordinate space, the symmetry force constants of SYMFFII which involve the O—CH_3 group were transformed into valence coordinate space. Certain assumptions, which generally vary with the model of the valence force field being used, must be made because of the angular redundancy [28]. These assumptions are in addition to the ones which have been made in the constrained symmetry force field, i.e., which were necessary because the data were insufficient to obtain values for all independent force constants. This first set of assumptions is reflected in Table 4. It involves the neglect of some off diagonal terms in the $\mathcal{F}$-matrix and the assumption that $\mathcal{F}$-constants for CH_3 rocking and asymmetric bending modes have identical values for in-plane and out-of-plane vibrations. To arrive at a set of valence force constants, the following model was adopted: all three HCH bending constants and OCH bending constants have identical values; there are no interaction terms between HCH bending constants ($f_{\alpha,\alpha} = 0$); no interaction terms between HCH and OCH bending constants ($f_{\alpha,\beta} = 0$). (The assumption that rocking and bending $\mathcal{F}$-constants are equal for a' and a'' modes was already made in the $\mathcal{F}$-matrix). Based on such a model the valence constants obtained from the **U**-matrix (Table 3) and the $\mathcal{F}$-constants (Table 4) are given in Table 7. Two interaction terms involving C—OCH_3 stretching must be included because of the interaction between CH_3 in-plane rocking and C—OCH_3 stretching [$F(8, 10)$]. The symmetry force constants involving the H(CO)O grouping were not transformed because the choice of individual bending constants would be quite arbitrary.

[32] T. Shimanouchi, I. Nakagawa, J. Hiraishi and M. Ishii, *J. Mol. Spectry* **19**, 78 (1966).

Table 7. Valence force constants for the OCH_3 group from SYMFFII. Nomenclature based on Fig. 2

$F_5 \equiv F_6$	4.927	$f_{5,6}$	0.107
F_7	4.977	$f_{5,7} \equiv f_{6,7}$	0.057
F_α	0.517	$f_{4,\beta(1)}$	0.589
F_β	0.856	$f_{4,\beta(2)} \equiv f_{4,\beta(3)}$	0.339
		$f_{3,\beta(1)}$	0.182
		$f_{3,\beta(2)} \equiv f_{3,\beta(3)}$	−0.091
		$f_{\beta,\beta}$	−0.015

Potential energy distribution and Cartesian displacements

Table 8 presents the approximate potential energy distribution (PED) [33] of the normal modes of formic acid in terms of symmetry coordinates. (The essentially pure CH and OH stretching modes are not included; neither are the columns corresponding to the off diagonal elements, $S_{i,j}$). Corresponding data on the

Table 8. Approximate potential energy distribution,* HCOOH. Upper value: SYMFFI. Lower value: SYMFFII

	S_4 (C=O s)†	S_7 (H—C r)	S_{14} (COH b)	S_9 (C—O s)	S_{11} (OCO b)	S_{18} (H—C γ)	S_{21} (COH τ)
ν_3	0.82	0.02	0.04	0.17	—		
	0.85	0.07	0.03	0.17	0.01		
ν_4	—	0.93	0.03	0.10	0.02		
	—	0.91	0.05	0.01	0.01		
ν_5	0.18	0.11	0.60	0.06	—		
	0.17	0.03	0.46	0.27	—		
ν_6	0.01	0.03	0.17	0.47	0.32		
	0.01	0.04	0.27	0.47	0.28		
ν_7	—	—	0.17	0.25	0.69		
	—	0.01	0.23	0.12	0.74		
ν_8						1.08	0.02
						1.08	0.02
ν_9						0.05	1.11
						0.05	1.11

* ν_1 and ν_2 are almost pure OH and CH stretching modes (0.99, 0.98).
† Approximate description. See Table 3.

in-plane modes of methyl formate are given in Table 9. The out-of-plane modes of methyl formate are essentially pure, except for ν_{14} and ν_{15}. ν_{14}: 0.84 S_{16}, 0.14 S_{17}. ν_{15}: 0.14 S_{16}, 0.84 S_{17}. (cf. Table 3).

The data presented in Tables 8 and 9 illustrate the usefulness as well as the limitations of PED as a way to characterize complex group vibrations. Separable modes (such as ν_4 of HCOOH and ν_4–ν_7 of $HCOOCH_3$) are clearly identified. Differences in calculated normal coordinates resulting from different approximations in the employed force field are also reflected in the potential energy distribution. The distribution obtained for ν_5 of HCOOH with SYMFFI and SYMFFII (Table 8), and for ν_8 of $HCOOCH_3$ (Table 9) provide relevant examples.

[33] Y. Morino and K. Kuchitsu, *J. Chem. Phys.* **20**, 1809 (1952).

While some information is obtained regarding the "purity" of a group vibration, and about the effect of different approximate force fields, PED provides little insight into the nature of complex modes involving several internal displacement coordinates, such as ν_8, ν_{10} and ν_{11} of $HCOOCH_3$. Presentation of the atomic displacements in Cartesian coordinates, on the other hand, does provide information about the nature of these mixed modes.

The Cartesian displacements (from SYMFFII) for some of the less obvious a' vibrations of HCOOCH, DCOOD, $HCOOCH_3$ and $DCOOCD_3$ are shown in Figs. 3 and 4. In these figures the coordinate system has been rotated about a vertical axis by six degrees. The displacements are drawn to the same scale as the equilibrium geometry and represent unit changes in the normal coordinates. We note

Table 9. Approximate potential energy distribution, $HCOOCH_3$ in-plane modes.*
Upper value: SYMFFI. Lower value: SYMFFII

	S_4† (C=O s)	S_5 (CH_3 ab)	S_6 (CH_3 sb)	S_7 (H—C r)	S_8 (CH_3 r)	S_9 (C—O s)	S_{10} (O—CH_3 s)	S_{11} (OCO b)	S_{12} (COC b)
ν_4	0.88	—	—	0.01	—	0.16	—	—	0.01
	0.89	—	—	0.08	—	0.16	—	—	0.02
ν_5	—	0.82	0.02	0.01	0.14	—	—	—	—
	—	0.82	0.02	—	0.16	—	—	—	—
ν_6	—	0.02	1.03	—	—	—	0.01	—	—
	—	0.02	1.03	—	—	—	0.01	—	—
ν_7	0.01	0.02	—	1.00	—	0.08	—	0.02	—
	0.03	—	0.01	0.93	—	0.01	—	—	—
ν_8	0.11	0.01	0.04	0.05	0.06	0.27	0.24	0.24	0.07
	0.06	0.06	0.01	—	0.20	0.49	0.18	0.12	—
ν_9	0.01	0.11	—	—	0.75	0.11	0.04	—	0.03
	—	0.09	0.02	—	0.57	0.09	0.05	0.12	0.08
ν_{10}	0.07	0.01	0.01	0.01	—	0.33	0.39	0.02	0.15
	0.03	—	0.02	0.02	—	0.25	0.57	0.03	0.12
ν_{11}	—	0.01	0.01	0.01	0.06	0.01	0.40	0.43	0.13
	0.01	0.01	—	—	0.08	0.01	0.29	0.45	0.14
ν_{12}	—	—	—	—	0.03	0.09	0.02	0.30	0.59
	—	—	—	—	0.01	0.02	—	0.29	0.65

* The CH stretching modes ν_1, ν_2, ν_3 are essentially pure.
† See Table 3.

in Fig. 3 that ν_5, ν_6 and ν_7 of $HCOOCH_3$ may be reasonably described as "antisymmetric CH_3 deformation", "CH_3 umbrella deformation," and "CH rocking" respectively. But, in the fully deuterated molecule, the "antisymmetric CD_3 deformation" couples with the "CD rock" of the DCOO group (ν_7, ν_8). This behavior contrasts with that of the $HCOOCD_3$ and $DCOOCH_3$ molecules where the "CD_3 antisymmetric deformation" (1050.7 cm^{-1}) is reasonably pure and the "CD rock" (1055.2 cm^{-1}) couples with a symmetric C—O—C stretch (878.7 cm^{-1}). This latter coupling is also evident between ν_8 (1041.4 cm^{-1}) and ν_{10} (837.8 cm^{-1}, Fig. 4) of the $DCOOCD_3$ molecule.

The ν_8 vibration (1219·5 cm^{-1}) of the $HCOOCH_3$ molecule gives rise to a very strong infrared band which is characteristic of many esters and it appears, from Fig. 3, that this mode can be simply described as an antisymmetric C—O—C stretch which, in this case, is coupled to the CH_3 rocking coordinate. The degree of coupling is not certain as seen by the variation in the PED (Table 9, ν_8).

The ν_{10} vibration (927.5 cm^{-1}) of $HCOOCH_3$ appears to be an ideal "symmetric

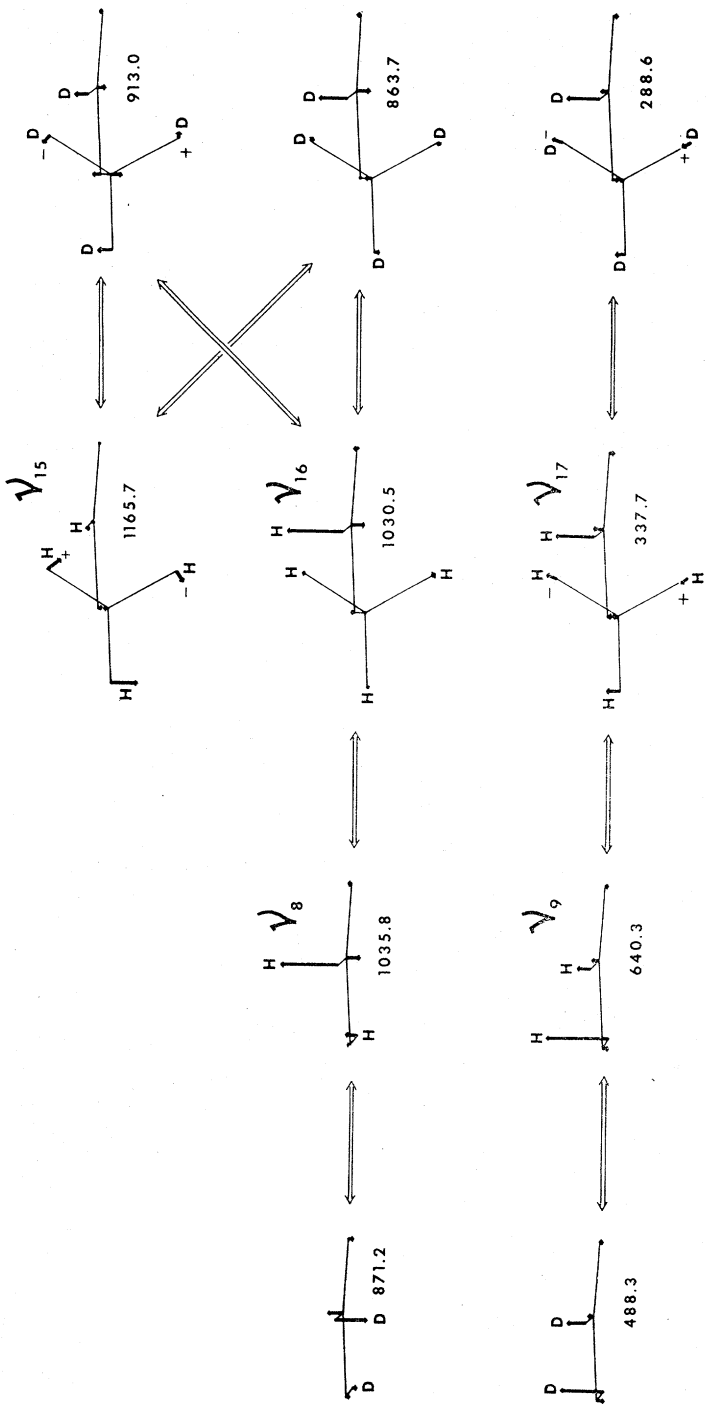

Fig. 5. Cartesian displacements for some out-of-plane modes as viewed approximately along the CH_3—O (or OH) bond, based on SYMFFII. Broad arrows and +, − signs as in Fig. 3.

C—O—C stretch" (≈70% CO stretch on PED) and it would seem that this vibration might be very characteristic of methyl esters. The O—C—O bending co-ordinate appears to be particularly important on the ν_{11} vibration of $HCOOCH_3$ (772.7 cm^{-1}) and $DCOOCD_3$ (707.5 cm^{-1}) and confirms the choice of symmetry bending co-ordinates made earlier. The corresponding vibration in HCOOH appears at a lower frequency (632.9 cm^{-1}) because of the lack of interaction with CH_3—O stretch.

Some out-of-plane vibrations are shown in Fig. 5. The view is from the methyl group end ($HCOOCH_3$) and approximately along the Me—O bond. The out-of-plane hydrogen deformation of the HCOO group and the twisting vibration of the O—C—O—CH_3 framework is evident in these figures. A coupling between the D deformation (DCOO) and CD_3 rocking coordinates is evident in the ν_{15} and ν_{16} vibrations of $DCOOCD_3$.